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INORGANIC PHOTOTROPIC MATERIALS FOR HIGH DENSITY COMPUTER MEMORIES

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FOREWORD

This report was prepared by the Chemical Research Department of Polacoat Incorporated, 9750 Conklin Road, Blue Ash 42, Ohio, under Air Force Contract No. AF 33(616)-7333, Project No. 7062 and Task No. 706201. The work was administered under the direction of the Electronic Technology Laboratory, Aeronautical Systems Division. Mr. Thomas S. Gerros, Electronic Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, initiated the contract.

This contract was under the general supervision of John Dreyer, Director of Research and Robert Harries, Head of Chemical Research Department, Polacoat Incorporated.

This specific research effort was under the leadership of Mr. Richard Radler with the following members of the Chemical Research Department having cooperated in the research for this report: Mr. G. Chaney, Mr. C. Noble and Mr. J. Gouge.

This report covers the work conducted from 1 January 1961 through 31 December 1962.

ABSTRACT

This report presents the results of a continuing research program in the synthesis, evaluation and application of inorganic "F" center type phototropic systems for use in bi-optic high density storage media for computer memories.

The results of an extensive synthesis and evaluation program to prepare synthetic hackmanite type materials and tenebrescent glass materials are given along with some application concepts.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

for *James R. Moore*
LEONARD M. BUTSCH, JR.

Lt. Colonel, USAF
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TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
1. INTRODUCTION	1
2. SOLID STATE SYNTHESIS	2
2.1 ADDITIONS OF BORIC OXIDE AND SILICA	2
2.2 SCREENING EXPERIMENTS	11
2.3 ADDITION OF SODIUM SULFATE (Na_2SO_4)	19
2.4 INCOMPLETE REACTION CONSIDERATIONS (THE GREEN MATERIAL)	20
2.5 ADDITIONS OF SODIUM BORATE ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)	23
2.6 ADDITION OF EXCESS SODIUM HYDROXIDE (NaOH) AND SODIUM CARBONATE (Na_2CO_3)	24
2.7 ADDITION OF TRISODIUM PHOSPHATE ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	24
3. PREPARATION IN A MOLTEN MEDIA	24
4. PREPARATION OF TENEERESCENT GLASS MATERIALS	25
5. PREPARATION OF TRANSPARENT COATINGS OF SYNTHETIC HACKMANITE	26
6. BARIUM FLUORIDE AND CALCIUM FLUORIDE INVESTIGATION	27
7. COMPUTER APPLICATIONS	28
8. CONCLUSIONS	29
REFERENCE LIST	30

LIST OF ILLUSTRATIONS

<u>FIGURE NO.</u>		<u>PAGE</u>
1.	Energy Level Diagram for Fluorescence	21
2.	Energy Level Diagram for White Tenebrescent Material	21
3.	Energy Level Diagram Showing the Coloration Reaction	22

LIST OF TABLES

<u>TABLE NO.</u>		<u>PAGE</u>
1.	Basic Hackmanite Type Compositions	3
2.	Firing Treatment of Nonuniform B_2O_3 Hackmanite Compositions	4
3.	Table Showing the Formulations of Various Hackmanite Compositions	6
4.	Table Showing the Effect of Varying the Amount of Sulfate with a Constant Concentration of B_2O_3	8
5.	Composition to Which Silicic Acid Was Added to H-11-S-3	9
6.	Tabulation of Experiments Dealing with the Addition of Various Substances of the Basic 2A+ Composition	13
7.	Table Giving the Results of Refiring Na_2SO_4 Rich Compositions	19

INORGANIC PHOTOTROPIC
MATERIALS FOR HIGH
DENSITY COMPUTER MEMORIES

1. INTRODUCTION

The purpose of this research project was to determine the applicability of the phototropic phenomenon and materials to memory devices for the high density storage of computer data. Accordingly, this project was divided into two phases; first, a general investigation of various types of phototropic phenomena as applied to a memory device, and secondly, to synthesize, evaluate and obtain techniques for the use of these materials in a memory device.

Previous research studies (see ref. 1) have shown that inorganic F center tenebrescent materials appeared to have most promise of meeting the requirements for a bi-optic computer storage device. As a result, the major portion of this effort was directed towards the synthesis and evaluation of these materials. The parameters for a bi-optic computer storage device are as follows:

- a) The system must have two stable states (i.e., colored and colorless).
- b) The system must be capable of being switched, at will, from one stable state to another, preferably by means of electromagnetic radiation of two different wavelengths.
- c) The system should have well defined, narrow activation, reading, and de-activating wavelength regions.
- d) The system should be capable of being read at a wavelength where the spectral absorption characteristics provide a maximum difference and does not induce a change from one state to the other.
- e) The change in the absorption, transmission, or reflected properties of the system should be such as to give a contrast ratio of at least 3-1 (preferably higher).
- f) The response speed of the activation or forward reaction, as well as that of the erase or back reaction, should be in the neighborhood of 0.1 to 1.0 microseconds or less.

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- g) As a maximum, the system should be capable of 10^6 reversals between the two states while not exhibiting any breakdown or fatigue. As a minimum, the system should have no more than 10 percent breakdown in a 300 hour period.
- h) The energy required for inducing the required change from one state to the other should be relatively small.
- i) The system should be easily incorporated into a wide area (e.g., sheet form) or on some type of inert media (e.g., plastic or glass).
- j) In the wide area form, the system should be capable of storing 10^6 bits of information per square inch.

2. SOLID STATE SYNTHESIS

A major portion of the synthesis work was performed using the general method of solid state high temperature reaction at atmospheric pressure. Particular emphasis was placed on temperature, addition of fluxes or glass forming material, and on the actual firing procedure. This work is described below.

2.1 ADDITIONS OF BORIC OXIDE AND SILICA

As reported in the initial report concerning hackmanite type materials (see ref. 1), the tenebrescent property was destroyed when temperatures above 1000°C were obtained. Sodium chloride could easily be lost at these temperatures due to its volatility. To support this view, it was shown that several samples that were not photosensitive after long firing times, could be made tenebrescent by remixing the material with additional sodium chloride followed by a firing treatment in a reducing atmosphere. Accordingly, three experimental procedures presented themselves as possible means of obtaining glass-like systems. Flux materials, such as boric oxide, sodium phosphate, or others could be added to lower the melting point. A molten material could be formed which would allow more complete reaction. This would produce larger areas of transparent hackmanite or disburse the hackmanite in a transparent glass matrix. Conceivably, a second method using mechanical means could be devised by which the sodium chloride or other volatile components could be contained while firing at the high temperatures. Still a third possibility would be to form the hackmanite at lower temperatures using a hydrothermal or hot pressing technique.

The first possibility was extensively studied. One of the most promising materials used was boric oxide. In order to study the effect of the boric oxide on the color center formation, a composition of H-11-S-3 was prepared (see table 1) in such a way that the boric oxide was nonuniformly disbursed throughout. Samples of this material were fired as indicated in table 2.

TABLE 1
BASIC HACKMANITE TYPE COMPOSITIONS

COMPOSITION DESIGNATION	CHEMICAL FORMULA	PREPARATION PROCEDURE
H-11	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	Air fired the proper amounts of Na_2CO_3 , Linde A type Al_2O_3 and Mallinckrodt silicic acid three times in air at 900-1000°C
H-11-S-3	$3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) 1/2 \text{NaCl} \cdot 1/6 \text{Na}_2\text{SO}_4 + \text{B}_2\text{O}_3$	Mixed together 19 gm H-11, 1.24 gm NaCl, 0.67 gm Na_2SO_4 and 1.0 gm B_2O_3
2A	$3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \text{NaCl} 1/2 \text{Na}_2\text{SO}_4$	Air fired the proper amounts of Na_2CO_3 , Linde A type Al_2O_3 , Mallinckrodt silicic acid, NaCl and Na_2SO_4
2A+	---	2.0 gm 2A + 0.2 gm silicic acid. This was mixed together but was not given an additional firing treatment.

The H-11-S-3-4 resulted in a light gray material which had a glassy coating on the outside surface but only certain areas on the inside of the pellet were photosensitive. However, the physical appearance of the inside surface was uniform and no B_2O_3 rich sections could be observed. The only difference between H-11-S-3-4 and H-11-S-3-5 was that the latter showed less photosensitivity. Sample H-11-S-3-2 was a porous low density material with melted pocks present which were due to localized areas rich in B_2O_3 . The entire material turned pink on exposure to ultraviolet with the pocks turning darker than the rest of the material. Sample H-11-S-3-3 was exactly the same

TABLE 2

FIRING TREATMENT OF NONUNIFORM
B₂O₃ HACHIMANITE COMPOSITIONS

EXPERIMENT DESIGNATION	FIRING TREATMENT
H-11-S-3-1	Fired in H ₂ @ 1000°C for 1 hr.
H-11-S-3-2	Fired in H ₂ @ 1127°C for 1 hr.
H-11-S-3-3	Fired in H ₂ @ 1127°C for 2 hrs.
H-11-S-3-4	Fired in H ₂ @ 1226°C for 1 hr.
H-11-S-3-5	Fired in H ₂ @ 1226°C for 2 hrs.

as H-11-S-3-2 in physical appearance, differing in that only the pocks turned dark on exposure to ultraviolet. This color was identical to the color of the pocks in H-11-S-3-2. The material fired at the lowest temperature (H-11-S-3-1) was the most porous but also had melted pocks present which turned darker than the unmelted part. As a whole, this material developed more color than the other four samples.

The results with this series of experiments almost conclusively can be explained on the basis that the sodium chloride or other volatile component is lost at the higher temperatures and that the boric oxide flux action retarded this loss. To definitely prove this beyond any doubt, it would merely be necessary to refire some of the less active materials in an excess of sodium chloride. Previous experiments have indicated that such treatment regenerated photosensitive materials. The next consideration was to determine the optimum amounts of these compositional materials.

On firing a sample of H-11 in hydrogen at 1100°C for $\frac{1}{2}$ hour, the resultant substance did not show photosensitivity, indicating that H-11 alone was not sufficient for the tenebrescent response. By adding sodium chloride to H-11 and following this by firing in a reduced atmosphere, it was found that some color was developed upon exposure to ultraviolet. Even though the coloration was slight, it can be stated that sodium sulfate (Na₂SO₄) or sodium sulfide (Na₂S) is not required to induce the photo response. Since previous experiments usually contained sulfate or sulfide, sodium sulfite was added to the H-11 + NaCl material followed by firing at 1100°C in a reducing atmosphere. On exposure to ultraviolet, this material became colored.

Several experiments were then run in which boric oxide was added to form compositions similar to the H-11-S-3 discussed above. The aim here was to determine the optimum amounts of NaCl, Na_2SO_4 and B_2O_3 required to produce a satisfactory tenebrescent material with transparent qualities.

The first series of experiments consisted of adding B_2O_3 to a 2A composition along with additional amounts of NaCl. Some of the compositions are given in table 3. The results obtained indicate that as the amount of B_2O_3 is increased, the material becomes more glassy. Also, as the temperature is increased as was the case for those compositions to which boric acid was added in place of boric oxide, the glassy phase was formed for lesser amounts of the boric oxide. This is understandable because the melting eutectic is lowered for those compositions which contain any amount of boric oxide.

Whether the melting or the presence of boric oxide is the cause of the loss of tenebrescence cannot be stated for certain. Previous work by Kirk and Medved (see ref. 3 and 4) indicates that the melting process changes the basic sodalite composition. Accordingly, this would indicate that this melting process would make the mechanism inoperative. Still another explanation was that the B_2O_3 could very easily react with the structure in such a way as to modify the system and thus ruin the tenebrescent property. Since small amounts of B_2O_3 did not appear to be detrimental, there probably was an optimum ratio of B_2O_3 to the 2A composition which will allow glass formation or increased reaction between the sodalite type crystals without the destruction of the tenebrescent quality. It is anticipated that extensive work will be carried out in this area but x-ray diffraction patterns would be required to ascertain the exact structural effect of B_2O_3 , firing conditions and other fluxing reagents.

In nearly every case, except those for which the amounts of B_2O_3 was about 0.05 grams, the substance resulting after firing had a yellow-green or green color and upon exposure to ultraviolet fluoresced. This was interpreted as caused by a reaction between B_2O_3 and Na_2S as described by Weyl (see ref. 2). Since it was previously shown (see ref. 1) that sulfide was not of critical importance to the formation of F centers in hackmanite, the amount of sulfide in this composition was reduced.

To accomplish this, varying amounts of Na_2SO_4 were added to H-11 while the amount of B_2O_3 was kept constant. The results of several of these experiments are shown in table 4.

Results obtained indicate that an optimum amount of Na_2SO_4 need not cause a green coloration but yet would still give a translucent material possessing a high degree of tenebrescence. This optimum

TABLE 3

TABLE SHOWING THE FORMULATIONS
OF VARIOUS HACKMANITE COMPOSITIONS

EXPERIMENT DESIGNATION	COMPOSITION	FIRE TREATMENT	RESULTS
H-76-6	2.0 gm 2A 0.05 gm B ₂ O ₃ 0.125 gm NaCl	Air fired for 10 min. @ 1000°C followed by hydrogen firing for 15 min. @ 1000°C	Excellent color change on exposure to ultraviolet. A green-yellow material resulted after firing which fluoresced under ultraviolet.
H-76-2	2.0 gm 2A 0.4 gm B ₂ O ₃ 0.125 gm NaCl	Same as H-76-6	A glass resulted that fluoresced slightly. No green color resulted after H ₂ firing. No color was developed on exposure to ultraviolet.
H-76-3	2.0 gm 2A 0.3 gm B ₂ O ₃ 0.125 gm NaCl	Same as H-76-6	A glassy material resulted that showed slight fluorescence. A slight green color was present after H ₂ firing. No color resulted on exposure to ultraviolet.
H-76-4	2.0 gm 2A 0.1 gm B ₂ O ₃ 0.125 gm NaCl	Same as H-76-6	A green dense material resulted after H ₂ firing which fluoresced slightly. The color developed on exposure to ultraviolet was about the same as H-76-6.
H-76-5	2.0 gm 2A 0.5 gm B ₂ O ₃ 0.125 gm NaCl	Same as H-76-6	A glassy material resulted that did not color on exposure to ultraviolet. Slight fluorescence was observed.

(TABLE 3 CONTINUED)

EXPERIMENT DESIGNATION	COMPOSITION	FIRE TREATMENT	RESULTS
H-76-1	2.0 gm 2A 0.2 gm B_2O_3 0.125 gm NaCl	Same as H-76-6	A green well sintered material resulted that did not color on exposure to ultraviolet but did fluoresce strongly. No glass resulted.
H-76-7	2.0 gm 2A 0.4 gm H_3BO_3 0.125 gm NaCl	Fired in hydrogen @ 1100°C for $\frac{1}{2}$ hour	A yellow-green glassy material resulted that fluoresced but no color was obtained on ultraviolet exposure.
H-76-8	2.0 gm 2A 0.05 gm H_3BO_3 0.125 gm NaCl	Same as H-76-7	A well sintered material resulted with some melting. Excellent color change on exposure to ultraviolet. No green resulted after H_2 firing.
H-76-9	2.0 gm 2A 0.3 gm H_3BO_3 0.125 gm NaCl	Same as H-76-7	A green glassy material resulted that fluoresced strongly. No color obtained on ultraviolet exposure.
H-76-10	2.0 gm 2A 0.2 gm H_3BO_3 0.125 gm NaCl	Same as H-76-7	Same as H-76-9
H-76-11	2.0 gm 2A 0.1 gm H_3BO_3 0.125 gm NaCl	Same as H-76-7	Very dense glassy type material which colored well on exposure to ultraviolet. This material was somewhat translucent.
H-76-12	2.0 gm 2A 0.50 gm H_3BO_3 0.125 gm NaCl	Same as H-76-7	A glass resulted that neither fluoresced nor turned color on ultraviolet exposure.

TABLE 4

TABLE SHOWING THE EFFECT OF
VARYING THE AMOUNT OF SULFATE WITH
A CONSTANT CONCENTRATION OF B_2O_3

EXPERIMENT DESIGNATION	COMPOSITION	RESULTS
H-11-S-1 *	1.8 gm H-11 0.125 gm NaCl 0.1 gm B_2O_3 0.151 gm Na_2SO_4	Center part was orange-green, outer part was cream to white. Inner part fluoresced but did not color on exposure to ultra- violet. The cream part turned color but did not fluoresce.
H-11-S-2	1.8 gm H-11 0.125 gm NaCl 0.1 gm B_2O_3 0.302 gm Na_2SO_4	The whole pellet was orange and fluoresced on exposure to ultra- violet. No color centers were generated.
H-11-S-3	1.8 gm H-11 0.125 gm NaCl 0.1 gm B_2O_3 0.067 gm Na_2SO_4	Excellent glassy translucent material with strong clear generation on exposure to ultraviolet.
H-11-S-4	1.8 gm H-11 0.125 gm NaCl 0.1 gm B_2O_3 0.01 gm Na_2SO_4	Similar to H-11-S-3 except color generation was somewhat less.

* All were fired in hydrogen at $1100^\circ C$ for $\frac{1}{2}$ hour.

situation seemed to be the case with experiment H-11-S-3. A note of caution should be introduced concerning the temperature reported for the above experiments. As is well known, the temperature control in any high-temperature study is critical and usually the better the control, the greater is the validity of the data. In the above work, a platinum-platinum rhodium thermocouple was placed on the inside of the furnace chamber and not on the inside of the tube near the samples being fired. Later in the program, a pyrometer was obtained and the temperatures read on the sample were generally two to three-hundred degrees centigrade higher than those indicated by the temperature on the dial supplied with the furnace. It was also found that the pyrometer readings could fluctuate 20-50 degrees without any variation in the temperature as read from the furnace indicator. As will be seen later, this temperature control was important in explaining still another

phenomenon. In the future, it will be necessary to compare the pyrometer readings with those from a thermocouple placed near the sample. Since B_2O_3 had imparted a glassy translucent character to the hackmanite materials, it was then of interest to add excess silica to these B_2O_3 compositions. Several of these experiments are listed in table 5.

TABLE 5
COMPOSITION TO WHICH SILICIC
ACID WAS ADDED TO H-11-S-3

EXPERIMENT DESIGNATION	COMPOSITION *	RESULTS
H-11-SI-1	2.09 gm H-11-S-3 0.05 gm Silicic acid	The outside surface had melted pocks present. Inside of the material was not melted but turned dark on exposure to ultraviolet.
H-11-SI-2	2.09 gm H-11-S-3 0.1 gm Silicic acid	About the same as H-11-SI-1
H-11-SI-3	2.09 gm H-11-S-3 0.2 gm Silicic acid	Material had a white bubble melted appearance and turned dark on exposure to ultraviolet.
H-11-SI-4	2.09 gm H-11-S-3 0.3 gm Silicic acid	Material melted to a greater extent than the H-11-SI-3. Very little F color was obtained.

* All were fired in hydrogen at 1100°C for $\frac{1}{2}$ hour.

The results of these experiments tend to indicate that the firing temperature was not the same as that used to fire the H-11-S-3 composition. However, the largest amount of silicic acid added did cause the material to melt more extensively. The silicic acid also seemed to give a milkier appearance rather than the translucent qualities obtained in the H-11-S-3 composition. This indicated that additional silicic acid does not react well with the other components at this low temperature (1100°C) and relatively short firing period. To check out the melting characteristics, therefore, samples of H-11, 2A and 2A+ (see table 1) were fired at various temperatures. The results indicated that the 2A+ composition melted at a lower temperature

than 2A or H-11 systems even at 1250°C. During the melting process, the 2A+ composition frothed extensively, which may indicate that further decomposition was taking place. It could, therefore, be concluded that the cloudy appearance of the H-11-SI series was due to the incomplete decomposition of the additional silicic acid. In future efforts, these compositions will be investigated with air firing before firing in the reducing atmosphere.

Still another synthesis procedure that gave fairly good results was in tightly packing the basic 2A composition into a Vycor tube and firing this in hydrogen at about 1100°C for $\frac{1}{2}$ hour. Since Vycor contains B_2O_3 in its composition, this method gave a glassy type material for that portion of the material in contact with the Vycor tube. The method was not easily controlled and was abandoned as not being practical.

The next procedure tried was to coat an alumina boat with boric acid, place the sample in it and fire in the furnace at 1000°C. A sample of 2A was pressed into a pellet and placed on top of the B_2O_3 layer. This was fired in a hydrogen atmosphere for $\frac{1}{2}$ hour at 1000°C. A resulting material with excellent tenebrescent properties was obtained in that part of the pellet which was between the outside surface in contact with the B_2O_3 and the center of the pellet to which the B_2O_3 had not diffused. The part of the pellet in contact with the B_2O_3 turned to a black glass. It was felt that the boat in a reducing atmosphere reacted with the B_2O_3 and the Na_2SO_4 and a new firing fixture was therefore required.

Graphite tubes closed at either end with tightly fitting graphite plugs were then used as the firing fixtures. This proved to be quite satisfactory in that there was no reaction between the graphite and the composition materials. This procedure also allowed for the material to be cooled to room temperature in a reducing atmosphere. This was later found to be of critical importance as the tenebrescent property was found to be destroyed if the hackmanite materials were placed in an oxidizing atmosphere while at temperatures above 400°C. This method of firing the materials was used almost exclusively for the remainder of the studies.

Approximately 2.0 gm of 2A+ was tightly packed into a graphite tube and fired at 1150°C for $\frac{1}{2}$ hour in hydrogen. The resulting material formed a melted opaque glass that became quite colored upon exposure to ultraviolet light. This material was then remixed in a mortar and pestle, additional amounts of NaCl added and again fired. After a total of three firings, a homogeneous opaque glass was formed that became darkly colored upon exposure to ultraviolet light. On exposure to white light, the bleaching reaction was found not to go to completion. It would completely reverse when the material was heated to temperatures

above 300°C. This method, therefore, allowed for the melting of the hackmanite material without the resulting loss of tenebrescent properties. It was previously reported that the material could not be fired above temperatures of 1050°C. Using this technique, temperatures of 1200°C were used without the loss of any tenebrescent characteristics. The effect of long time firing at these temperatures was not evaluated.

Since a temperature of 1200°C had been reached, it was of interest to fire the 2A+ at higher temperatures. Accordingly, a sample was placed in a graphite tube and fired in hydrogen at 1250°C. The material had completely melted and had a tan-colored glassy material disbursed throughout a clear glass matrix. This experiment indicated that 1200°C was the highest possible firing temperature.

A sample of 2A material, which had previously been fired at 1100°C in hydrogen, was mixed with an additional amount of NaCl and then fired at a temperature of 1300° to 1350°C for $\frac{1}{2}$ hour. The material completely melted and resulted in a smooth-surfaced pellet with a body material heavily populated with gas bubbles and possessing a light red color. On exposure to ultraviolet light, the material became quite dark and on exposure to a tungsten lamp, the color was nearly completely bleached.

In conclusion, it can be stated that materials with tenebrescent properties can and were prepared at temperatures as high as 1350°C. In some compositions, temperatures above 1250°C could not be used. This possibly indicates that, at higher temperatures, the presence of excess silica (sample 2A+) may be detrimental.

Two objectives were yet to be accomplished. One, to increase the speed of the fading reaction, and two, to obtain a transparent material. A screening type experiment was then undertaken to study the effects of different materials on both the tenebrescent and transparent characteristics of the synthetic systems.

2.2 SCREENING EXPERIMENTS

A series of experiments were run with the object of determining the effect of adding different materials to the 2A+ composition. This served primarily as a screening type experiment, in which the results observed were primarily 1) whether the added material destroyed the tenebrescent properties, 2) whether the added material had no effect on the tenebrescent properties, 3) whether it improved the obtainable color or the bleaching reaction, and 4) whether the transparent characteristics were improved.

A general procedure was followed for all of these experiments in which 2.0 grams of 2A+ was mixed with 0.125 grams of NaCl and a given amount of the material being studied. The mixture was then tightly packed into a graphite firing fixture and fired in a hydrogen atmosphere at 1100° to 1125°C for fifteen minutes. Results are shown in table 6. From the data obtained, several interesting conclusions were drawn from the experiments and some will be briefly commented on here while the total results will be discussed under succeeding parts of this report.

It appears as if the transition elements tended to turn the material dark after firing in a reducing atmosphere. Cadmium was the exception to this and it would be of interest to determine the underlying reasons. In the case of manganese (items 17 and 29), it was shown that the darkening was eliminated when the amount was reduced, but the tenebrescent characteristics were improved. It appeared that in the case of all compounds which caused darkening, concentration was an important factor. An interesting study would be to determine whether a correlation exists between the effects on tenebrescence and the number of unpaired electrons in the transition element. However, such a study should await the production of a transparent material.

In many cases, a green fluorescent material was obtained and it is enlightening to note that in most cases, boric oxide was not present. This would not agree with earlier conclusions which attributed the green color to a reaction between B_2O_3 and Na_2S . The green material always fluoresced, thus indicating a connection between this and the tenebrescent property. More will be said concerning this in a latter part of this report.

Lithium fluoride, sodium silico fluoride and calcium fluoride (items 6, 45 and 15) are interesting in that the addition of lithium fluoride and sodium silico fluoride induced a great amount of melting but destroyed the tenebrescent properties. This seemed to point to fluorine as the detrimental ion, but this was contradicted by the fact that calcium fluoride as the additive, did not destroy the tenebrescence. In the future, more work should be carried out with these and other fluorides since they are extensively used as mineralizers (see ref. 3).

The results obtained with the addition of sodium sulfate were interesting, in that they showed that excess sulfide did not have a detrimental effect.

All of the above data cannot be used as conclusive results since the experiments were designed primarily to give indications as to the direction for further experimental efforts. Since the firing time was only 15 minutes, for all practical purposes, the final material

TABLE 6
TABULATION OF EXPERIMENTS DEALING
WITH THE ADDITION OF VARIOUS
SUBSTANCES OF THE BASIC 2A+ COMPOSITION

ITEM NO.	EXPERIMENT NUMBER	MATERIAL AND AMOUNT ADDED	RESULTS
1	81762-1	0.2 gm Na_2CO_3	The material had an orange color but did not have a green color after firing. On exposure to ultraviolet the material darkened somewhat.
2	81762-2	0.1 gm K_2CO_3	The characteristics were similar to 81762-1. This is interesting since K was used in place of Na. Further work should be carried out with the addition of potassium salts to check change in absorption characteristics.
3	81762-3	0.1 gm CaNO_3	Same results and conclusions as 81762-2.
4	81762-4	0.1 gm NaNO_3	Similar to 81762-1.
5	81762-5	0.1 gm NaOH	Similar to 81762-1 except less color was developed on exposure to ultraviolet.
6	81762-6	0.1 gm LiF	No color was obtained on exposure to ultraviolet. The density to which the material fired was excellent. In many previous experiments the LiF salt always seemed to aid in the densification but the color center phenomenon was always destroyed. It is difficult to say whether in this case the Li or F ions are the cause of destruction of tenebrescence. Experiments should be carried out using Li_2CO_3 and NaF separately as additives.
7	81762-7	0.1 gm Na_2SO_4	On exposure to ultraviolet the surface only turned colored and the bleaching was quite good. The material was quite heterogeneous in appearance, the inside part being green. This material should be remixed and refired.

(TABLE 6 CONTINUED)

ITEM NO.	EXPERIMENT NUMBER	MATERIAL AND AMOUNT ADDED	RESULTS
8	81762-8	0.2 gm Na_2SO_4	Similar to 81762-7 except the color after firing on the inside of the material was somewhat green.
9	81762-9	0.3 gm Na_2SO_4	Appears to be too great an excess. Further work should be conducted using excess Na_2SO_4 .
10	81762-10	0.1 gm sulfur	Similar to 81762-1.
11	81562-7	0.1 gm MgO	A material with a light gray vitreous surface and a vitreous inside with a dark green color was obtained. On exposure to ultraviolet only the gray part colored. The green part fluoresced greatly.
12	81562-5	0.1 gm CaO	Similar to 81562-7 except the green color was lighter.
13	81762-11	0.1 gm SrCO_3	Similar to 81762-1.
14	81762-12	0.1 gm Mg	Similar to 81762-1. This material was not like 81562-7 as far as the melting characteristics are concerned. This material should be ground and refired. Probably MgO should be studied in place of Mg .
15	81762-13	0.1 gm CaF_2	Similar to 81762-1. Here the F did not destroy the tenebrescence (see exp. 81762-6). This would indicate that F does not necessarily destroy tenebrescence and should be studied further.
16	81762-14	0.1 gm $\text{Ba}(\text{OH})_2$	Similar to 81562-7. This should be investigated further.
17	81762-15	0.1 gm MnO_2 (Equivalent to 0.066 gm of Mn)	The material turned dark on firing and therefore masked the color change on exposure to ultraviolet. MnO_2 in reduced atmospheres turns dark and therefore only very small amounts of this can be added.

(TABLE 6 CONTINUED)

ITEM NO.	EXPERIMENT NUMBER	MATERIAL AND AMOUNT ADDED	RESULTS
18	81762-16	0.1 gm GeO ₂	Similar to 81762-15.
19	81762-17	0.1 gm In ₂ O ₃	Similar to 81762-15.
20	81762-18	0.1 gm ZnO	Slight color change on exposure to ultraviolet. From this one experiment it appears that ZnO destroys color and should probably be avoided.
21	81762-19	0.1 gm SnSO ₄	Similar to 81762-15.
22	81762-20	0.1 gm PbO	Similar to 81762-15.
23	81762-21	0.1 gm NiCO ₃	Similar to 81762-15.
24	81762-22	0.1 gm Mo	Similar to 81762-15.
25	81762-23	0.1 gm CeO ₂	Similar to 81762-1. The back reaction was not too good but this material may be of interest with reference to ultra-violet absorption characteristics.
26	81762-24	0.1 gm Ce(NO ₃) ₄	Similar to 81762-23.
27	81762-25	0.1 gm CrCl ₃	Similar to 81762-15.
28	81762-26	0.1 gm Cr(Ac) ₃	Similar to 81762-15.
29	81762-27	0.1 gm Mn(C ₂ H ₃ O ₂) ₂ 4H ₂ O (Equivalent to 0.0024 gm of Mn)	Gave a good forward and fair back reaction. A gray color was obtained but the material was not nearly as dark as 81762-15. The amount of Mn added here is much less than 81762-15 and therefore very low concentration of manganese may be beneficial. More work should be carried out using this material and also the other transition metals.

(TABLE 6 CONTINUED)

ITEM NO.	EXPERIMENT NUMBER	MATERIAL AND AMOUNT ADDED	RESULTS
30	81762-28	0.1 gm $\text{FeCl}_3 \cdot \text{CH}_2\text{O}$	Similar to 81762-15.
31	81762-29	0.1 gm Fe	Similar to 81762-15.
32	81762-30	0.1 gm I ₂	Similar to 81762-1. The color developed on exposure to ultraviolet was not blue. NaI was previously found to give a blue coloration; therefore, it appears as if the I ₂ does not enter into the structure. It is probably of little value in these experiments.
33	81762-31	0.1 gm NaHS	Similar to 81762-1. This material should be incorporated in studies outlined for the Na_2SO_4 experiments (81762-7).
34	81762-32	0.1 gm CuO	Similar to 81762-15.
35	81762-33	0.1 gm $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	This material gave a good color change on exposure to ultraviolet. The reverse reaction was fair. This material did not fuse as much as desirable but nevertheless it should be investigated further.
36	81762-34	0.1 gm CdCl_2	No color was obtained on exposure to ultraviolet. This result indicates that there is a difference between this and 81762-33 and therefore this should be investigated further.
37	81762-35	0.1 gm BiCl_3	Gave a slight change on exposure to ultraviolet. The material had a dark green appearance after firing and this fluoresced to a limited extent.
38	81762-36	0.1 gm Bi_2O_3	Similar to 81762-1. Somewhat different results than 81762-35. This material did not increase the vitreous appearance and probably bismuth is of no value in these experiments.

(TABLE 6 CONTINUED)

ITEM NO.	EXPERIMENT NUMBER	MATERIAL AND AMOUNT ADDED	RESULTS
39	81762-37	0.1 gm SbS	Similar to 81762-15.
40	81762-38	0.1 gm $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	The material was green and seemed to have frothed on melting resulting in a translucent vitreous substance. Parts of the translucent material turned violet on exposure to ultraviolet. This should be investigated further.
41	81762-39	0.05 gm $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Similar to 81762-38 except that the material did not fuse to as great an extent.
42	8962-11	0.1 gm $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	An opaque glass type material was formed which turned very dark on exposure to ultraviolet and which had a very good back reaction. This material should be investigated further with special emphasis on the back reaction improvement.
43	81762-40	Several drops of H_3PO_4	Very little color was obtained on exposure to ultraviolet. The material frothed extensively during the firing treatment and a spongy glass resulted. This should be investigated in connection with experiment 8962-11.
44	H-82-1	0.05 gm AlCl_3	A material with a cream color resulted which had orange speckles throughout. Color similar to 81762-1 on exposure to ultraviolet resulted. This material does not seem of particular interest.
45	8962-7	0.1 gm Sodium Silica Fluoride	The material was very glassy and had a green color. On exposure to ultraviolet the material did not color but strong fluorescence was induced. This material is a very strong fluxing agent and possibly would be suitable in smaller quantities.

(TABLE 6 CONTINUED)

ITEM NO.	EXPERIMENT NUMBER	MATERIAL AND AMOUNT ADDED	RESULTS
46	8962-2	0.1 gm Sylvania Luminescent Chemical Type #170 $\text{CaMg}(\text{SiO}_3)_2:\text{Tl}$	The material was very glassy and in parts was transparent. On exposure to ultraviolet only the surface of the melt turned slightly pink, a strong fluorescence was observed. Should investigate this material further with special emphasis on its fluxing qualities.
47	8962-4	0.1 gm Sylvania Phosphor #221 (Zinc silicate)	A very white opaque melt was obtained with a slight green color on the inside. On exposure to ultraviolet the surface colored extensively while the inside fluoresced strongly. The ZnO probably plays the role of an opacifier and should not be used.

was a nonequilibrium state and could be used only as an indication of the reaction path. This led to an interesting postulate that the true hackmanite was a nonequilibrium material which had the structural defects required for tenebrescence and would lead to the conclusion that the conditions under which large areas can be prepared might necessitate the use of pressure. Of course, the main argument against such a postulate is the fact that Medved (see ref. 4) has been able to fire the material at about 950°C for as long as 24 hours. However, this temperature was nearly 200°C less than the temperature used to fire the compositions given in table 6. Also, he was never able to obtain large sections of the synthesized material. Following sections of this report deal with work connected with the results obtained in table 6.

2.3 ADDITION OF SODIUM SULFATE (Na_2SO_4)

Since it was shown in experiments 81762-7, -8 and -9 that excess Na_2SO_4 could be added to the basic 2A+ without complete deterioration of tenebrescence and since Na_2SO_4 had a low melting point (i.e., 884°C), it was conceivable that it could be used as a fluxing agent for the formation of large transparent areas of hackmanite type materials. Accordingly, each of the materials was crushed and ground in a mortar and pestle and each mixed with 0.15 gm of NaCl. The materials were tightly packed into a graphite tube and then fired for 15 minutes at 1150°C. The results obtained are shown in table 7.

TABLE 7

TABLE GIVING THE RESULTS OF
REFIRING Na_2SO_4 RICH COMPOSITIONS

EXPERIMENT NUMBER	MATERIAL REFIRED	RESULTS
9562-1	81762-7 plus 0.1 gm Na_2SO_4	A white opaque glassy type material with a uniform composition was obtained. On exposure to ultraviolet the material turned very dark. The bleaching reaction was not complete.
9562-2	81762-8 plus 0.2 gm Na_2SO_4	Similar to 81762-7 except the material was somewhat translucent.
9562-3	81762-9 plus 0.3 gm Na_2SO_4	Similar to 81762-8 except the material was quite translucent. The color change on exposure to ultraviolet was excellent.

As a result of this data, two very important considerations should be discussed at this point. First, this data shows that as the amount of Na_2SO_4 was increased, the translucent properties became more pronounced indicating that Na_2SO_4 was beneficial. Unfortunately, compositions with larger amounts of Na_2SO_4 were not prepared, so that it is impossible to predict the limiting obtainable results. This experiment should definitely be considered for future work. Still another concept would be to refire the materials an additional number of times with the object of improving the extent of reaction. Also, in all probability, a material with a higher density could be prepared, if these materials were reacted under pressure.

The second observation of importance was that the materials no longer had the green color normally produced after the subsequent heat treatment. The data indicates that on incomplete reaction, a green material is formed. Accordingly, several experiments were carried out to determine the parameters involved in this problem.

2.4 INCOMPLETE REACTION CONSIDERATIONS (THE GREEN MATERIAL)

In order to substantiate the postulate that incomplete reaction of reactants caused the production of a green fluorescent material, the following experiment was undertaken. A sample of 2A+ was mixed with excess NaCl tightly packed into a graphite tube and fired for 1 hour at 1125-1150°C in a hydrogen furnace. The resulting substance was a white porcelain type glass that had no green color whatsoever. On exposure to ultraviolet, the material turned dark, but was not exceptional in this respect. A similar composition was prepared, but the firing period was reduced to 10 minutes, after which time a porcelain material was again obtained. However, the inside of this material was green and fluoresced to a great extent. Accordingly, it was concluded that the green substance is a result of insufficient reaction. To further substantiate this, the green material was remixed with additional NaCl and fired as previously, but for a $\frac{1}{2}$ hour period. The resultant opaque glass had no green color and on exposure to ultraviolet, colored to a very dark purple. It is felt that this green coloration is probably due to some nonequilibrium state, either chemical, such as reduction, or transitional, such as a phase equilibrium.

If it can be assumed that there is a relationship between the fluorescent and the tenebrescent properties, then it would appear that fluorescence is due to the nontrapping of the excited electrons by a level higher than the initial ground state of the green material. If a band energy level diagram is drawn for the green material, it should appear as shown in figure 1. That is, the electrons have no allowable higher energy level in which they can be absorbed. The fluorescence radiation should correspond to the energy gap indicated and this can be determined by a study of the fluorescence spectrum.

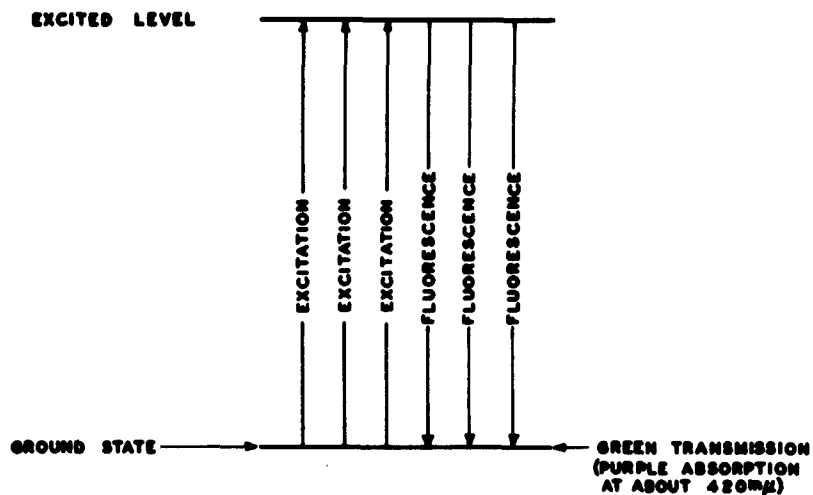


Figure 1. Energy Level Diagram for Fluorescence.

If a higher energy level is introduced into the material (i.e., by further reaction), it may be expected to have a white color due to the complementary absorption of color bands (see figure 2).

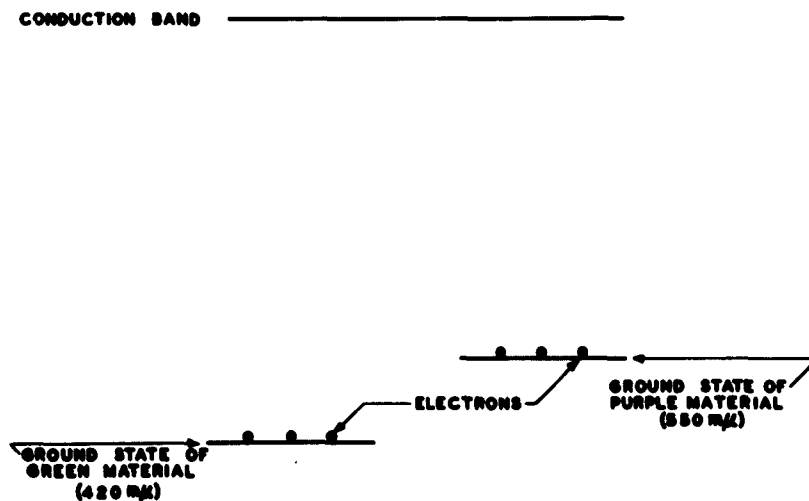


Figure 2. Energy Level Diagram for White Tenebrescent Material.

This added absorption band may then allow the excited electrons to be trapped as shown in figure 3 which would deplete the 420 mμ absorption band and increase the electron population of the 550 mμ absorption level. This would have the effect of upsetting the color complementation in favor of a purple color. To explain the absence of visible radiation, it would merely be necessary to state that the radiation is outside of the visible range and, therefore, cannot be observed with the eye.

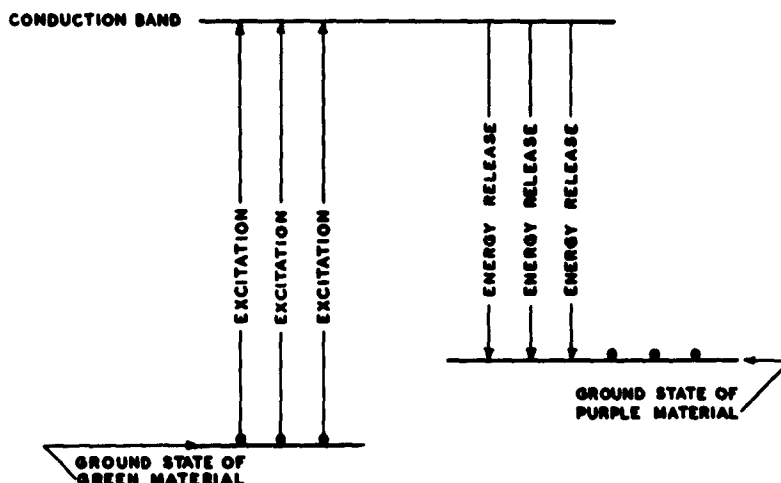


Figure 3. Energy Level Diagram Showing the Coloration Reaction.

Bleaching could then be explained on the basis that the electrons in the 550 mμ band absorb energy (radiation), allowing the electrons to enter the conduction band and then fall to the 420 mμ level. This picture may be used to explain why bleaching is sometimes difficult, if not impossible, since on bleaching, the electrons would have to be excited across the energy gap to the conduction level. If the bleaching energy is insufficient to allow this transition, the material won't be bleached. On the other hand, the usual sensitivity of the forward reaction can be explained by the fact that the ultraviolet is of sufficient energy to excite the electrons to the conduction level.

The above discussion may not be necessarily valid, but it indicates a possible avenue of investigation which may be fruitful in regards to understanding the basic mechanism involved and thus allowing the proper selection of doping agents.

2.5 ADDITIONS OF SODIUM BORATE ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)

The object of this series of experiments (see item #81762-39 of table 6) was to determine whether the fluxing action of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ could be used to lower the melting temperature of the material and to obtain a glass that would allow the active phase to be dissolved in the glass without destroying the tenebrescent properties. Still another role possible for this material would be to act as a mineralizer which would allow the hackmanite crystals to grow to a larger size.

The procedure was to add varying amounts of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ to the basic hackmanite starting compositions. These compositions were fired in a reducing atmosphere at about 1150°C for $\frac{1}{2}$ hour. After each firing cycle, the resulting material was ground in a mortar and pestle with excess NaCl and then refired.

It appeared that the reason for the green coloration, as reported above, was not due to the $\text{Na}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$ reaction, but rather to incomplete reaction. This pointed to a relation between the fluorescence and color center formation which will be investigated in the future.

After the first firing period, a green glassy material was obtained which showed strong fluorescence, but that did not change color. After the additional firing cycle, however, the green color disappeared and a white translucent material was obtained which darkened extensively on exposure to ultraviolet light. After polishing a section of the resulting material, it appeared as if the active particles were disbursed throughout a glass medium. The ratio of active particles to the glass matrix was quite large. With a high powered microscope and by the proper polishing of thin sections, it should be possible to determine exactly what type of structure was present.

Even so, these experiments showed that opacity could be reduced by the addition of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Accordingly, several more experiments were carried out which showed the synthesis to be critical to:

1. The amount of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.
2. The particular brand of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.
3. The firing treatment.

It should be pointed out that the addition of sodium borate not only introduces boric oxide but also increases the ratio of Na_2O to Al_2O_3 . The Al_2O_3 is believed to cause the opaque characteristics of the material so that as this component is reduced, the resulting melt should become more transparent.

2.6 ADDITION OF EXCESS SODIUM HYDROXIDE (NaOH) AND SODIUM CARBONATE (Na_2CO_3)

The object of these experiments was to determine the effect of increasing the Na_2O content through the addition of excess Na_2CO_3 and NaOH .

These materials did not show an increase in transparency or in the color developed as compared to those materials without excess Na_2CO_3 . The results obtained may be caused by the carbonate not being decomposed during the air firing prior to the reducing atmosphere firing.

Essentially the same procedure was followed for the additions of NaOH . Additions of NaOH definitely caused the material to take on an inherent tan color and, on exposure to ultraviolet, the NaOH rich material developed less color than that without the NaOH .

2.7 ADDITION OF TRISODIUM PHOSPHATE ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)

It was found that the addition of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ to the basic material resulted in a white opaque glass which, on exposure to ultraviolet light, turned very dark. The color, upon exposure to white light, faded much faster in this system than in the material without $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. On further experimentation, it was shown that the back reaction was indeed aided by the addition of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. However, a dark back reaction was also present which was effectively stopped by storing in very low temperatures.

A possible interpretation of these results would be that the phosphorous added tends to supply the material with the necessary impurity band required for a more sensitive bleaching reaction.

3. PREPARATION IN A MOLTEN MEDIA

As has been pointed out in the early part of this report, the loss of NaCl appears to be quite serious to the formation of F centers and a method of preparation preventing this loss would be desirable. To insure a rich NaCl reaction medium, several experiments were carried out with the objective of studying the possibility of using molten sodium chloride as the reaction medium for the preparation of tenebrescent hackmanite type compositions.

A mixture containing 2.0 grams of H-11, 0.15 grams of NaCl and 0.113 grams of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, which was identical to 2A, was prepared by grinding these components in a mortar and pestle. Using a hand

press, a pellet of this was formed and dropped into a crucible containing molten NaCl at 940°C. After fifteen minutes at this temperature, the crucible was placed into a furnace set at 500°C and allowed to cool for one-half hour. After this time, it was removed from the furnace and allowed to cool to room temperature.

Although the pellet was fired to a high density, on exposure to ultraviolet, tenebrescence was exhibited only on the inside center which turned dark. The outside part neither darkened nor fluoresced. In order to determine whether hydrogen firing would improve the tenebrescent properties, this pellet was fired at 1000°C in hydrogen for one-half hour. On exposure to ultraviolet, the obtainable color was slightly greater, but the entire pellet was colored.

A hydrogen fired pellet of 2A material showing tenebrescent properties, was then treated in a similar way. On exposure to ultraviolet light, this material possessed the same tenebrescent properties as before the molten salt treatment. A similar pellet was then allowed to fire in molten NaCl for one hour. As a result, the sodium chloride completely evaporated and the material showed no tenebrescent properties. Higher temperatures could not be used, as the maximum obtainable temperature of the furnace was 1000°C.

These experiments indicated that a tenebrescent material can be produced by firing the components in molten sodium chloride. Since it is difficult to prevent complete evaporation of the NaCl at temperatures above 1000°C, it will be necessary to design a heating system which will minimize this evaporation loss. Such a technique would allow the material to be melted in a sodium chloride medium and may prove to be quite interesting.

Other molten media such as barium chloride, sodium sulfite, and sodium sulfite plus NaCl were similarly investigated as molten media. Barium chloride gave results very similar to those of sodium chloride. However, with sodium sulfite, the material could be reduced since the sulfite reacts to form sodium sulfate and sodium sulfide on heating. When 2A was fired in molten sodium sulfite, a substance, which uniformly colored on exposure to ultraviolet, was obtained. This material should be investigated at higher temperatures and at temperatures nearer to the melting point of 2A.

4. PREPARATION OF TENEBRESCENT GLASS MATERIALS

Several glasses were prepared with the object of inducing tenebrescent properties.

The first glasses investigated were the low melting borates. Since it was shown that a halide was a requisite for the tenebrescence

phenomenon in hackmanite, several compositions of boric oxide, silica, and halides were investigated. In none of these was it possible to obtain color upon irradiation with ultraviolet light.

The next series of glasses tried were those prepared by a very high temperature firing of the basic hackmanite components. These did show tenebrescent properties. The tenebrescent characteristics could be modified by changing the basic composition. A detailed study of these glasses has not been completed and therefore results can be given with little explanation of the photosensitive mechanism. The following experimental procedure was utilized.

A two-gram sample of the H-11 material was tightly packed into a graphite tube and then slowly placed into a tube furnace modified to provide a nitrogen atmosphere. The graphite tube was allowed to fire at 2600-2800°F for four hours after which, it was removed and allowed to cool to room temperature while still in the graphite tube. On irradiation with ultraviolet light from a high pressure mercury arc for approximately one minute, the material turned yellow. This yellow glass could be stored for several weeks without fading. However, upon exposure to radiation of wavelengths longer than 350 mμ, the yellow color completely faded. The color could again be generated by exposure to the mercury arc.

Variations of the above composition were made and in some cases, the color characteristics obtained upon exposure to ultraviolet light were different.

Composition 2A was fired using the above procedure. On exposure to the mercury arc, this material turned a reddish-brown color which could not be made to bleach when exposed to longer wavelength radiation. However, on heating the colored materials to temperatures above 300°C, the glass was readily bleached.

Composition 2A+ was also melted into a glass, which on exposure to the mercury arc or sunlight, turned yellow. On exposure to wavelengths longer than 500 mμ, this glass was partially bleached.

A sample of natural hackmanite was ground in a mortar and pestle and fired as described for other glasses. This formed a transparent glass that turned yellow on exposure to the mercury arc. On exposure to white light, only partial bleaching could be affected. Heating the material to temperatures above 300°C did completely bleach the color.

5. PREPARATION OF TRANSPARENT COATINGS OF SYNTHETIC HACKMANITE

In an attempt to prepare transparent coatings of synthetic hackmanite, several attempts at matching refractive index of the plastic

matrix with the hackmanite material were made. After grinding the above described synthetic opaque glass hackmanite material in a mortar and pestle, it was placed into a ball mill and isopropyl alcohol was added to make a slurry of water consistency. This mixture was allowed to mill for at least 48 hours, after which time the slurry was poured into a cylinder such that microscope slides could easily be dipped into the slurry. Accordingly, several coatings were made on glass slides, each coating being allowed to dry before the successive coating was added. After the final coating was dried, the milled hackmanite was removed from one side of the slide. The slide containing the hackmanite was then coated with plastic by pouring a 60% acryloid solution (refractive index of 1.49357 measured with the sodium 539 mμ line at 26°C) over the hackmanite. As soon as the acryloid wetted the hackmanite particles, they became transparent. A second slide was then placed over the acryloid to prevent evaporation of the toluene which was used as the solvent for the acryloid resin. When this sandwiched coating was exposed to ultraviolet, it was colored to the usual hackmanite shade. On exposure to white light, the color completely bleached.

If the solvent was allowed to evaporate, the hackmanite coating again became opaque. Therefore, a resin with the refractive index of the 60% acryloid solution is required to make a transparent coating of this ball milled material.

6. BARIUM FLUORIDE AND CALCIUM FLUORIDE INVESTIGATION

Samples of barium and calcium fluoride were irradiated with gamma rays at an intensity of 2×10^5 roentgens for a period of one hour. The calcium fluoride showed essentially the same peaks after gamma irradiation as it did after x-ray exposure. That is, a peak was developed at approximately 400 mμ in both cases. This was the only peak developed, but according to literature, three other peaks should also have been developed. Before either x-ray treatment or gamma ray exposure, a peak at 580 mμ was present. This peak did not seem to increase nor decrease with this high energy irradiation.

The calcium fluoride crystal was then exposed to the 405 mμ spectral line of a mercury arc for a period of 2½ hours. The intensity of this source has not been determined. After this period of exposure, the peak at 400 mμ had definitely been bleached. It is difficult to say with certainty, but it also appears as if the absorption band at 580 mμ faded to a degree and a new band at approximately 480 mμ began to develop. This is in accordance with the results reported by Smakula (see ref. 5).

After the exposure to 405 mμ radiation, the sample was then exposed to the 580 mμ spectral line of the mercury arc for a period

of $5\frac{1}{2}$ hours. The sample then showed an increase of absorption at 400 mμ although this was very slight. It is difficult to say whether or not this peak at 480 mμ decreased and that at 580 mμ increased.

In conclusion, it can be stated that calcium fluoride does show the phenomenon described by Smakula, but with the sample investigated, these absorption band changes were too slight to be of value as a computer memory device. It would seem, however, that the magnitude of these absorption bands could be increased by the proper doping of the crystals. With increased sensitivity, this material could possibly be useful as a bi-optic memory material.

On exposure to x-rays, the barium fluoride did not appear to cause the development of absorption bands. However, on gamma ray exposure, the barium fluoride sample developed bands at about 1000 mμ, 700 mμ and 530 mμ. As in the case with calcium fluoride, the absorption bands were only slight. The effect of exposing the barium fluoride to different wavelengths of radiation has not as yet been investigated. In conclusion, it can be stated that x-ray exposure was not sufficient to develop absorption bands in the BaF₂ crystal, but gamma irradiation did induce absorption bands.

7. COMPUTER APPLICATIONS

During this research effort, a sample of natural hackmanite was subjected to approximately 400,000 cycles with little apparent fatigue. After this number of reversals, the sample did begin to deteriorate, but this could be attributed to a build up of temperature within the test device. Even so, after 500,000 cycles, the material still showed tenebrescent properties.

Some preliminary work was performed to determine the resolution characteristics of the previously described ball milled hackmanite coatings. The procedure used was to focus the light from a xenon lamp onto the coating with a camera lens. The smallest spot obtainable was approximately 1/32 of an inch. However, the resolution of the focused light was no better than 1/32 of an inch and, therefore, it is likely that if a smaller image were focused on the coating, the resolved spot would be less than 1/32 of an inch. It is felt that resolution studies can be made much easier by outside organizations interested in the computer application than by Polacoat. Accordingly, some samples were sent to them for this purpose. No results have as yet been obtained. In order to utilize tenebrescent materials in an optical memory device, consideration was given to several optical concepts and the problems involved. A survey of the availability of the components required for the read, write and erase functions of such a system has been undertaken. Consideration

was given to fixed lamp sources such as xenon lamps, lasers, and to flying spot scanners, moving mirrors, servo systems, Kerr cells, fiber optics, phosphors and their application to the problem. Several manufacturers of flying spot scanners were contacted and it appears that several could design such units. For reading and erasing, it would be necessary to use different phosphors for the cathode ray tube coating. These are also available. One commercial organization has an optical computer device, the light source of which, they feel could be modified for our purposes.

8. CONCLUSIONS

An opaque glass showing the hackmanite tenebrescent properties was prepared by firing the basic components at temperatures above 1150° . The bleaching reaction was found to be improved by the addition of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and a glass-like material could be made quite translucent by the addition of sodium borate. It is possible that these translucent glasses can be made transparent by hot pressing techniques; this should definitely be investigated. The addition of many other materials to the basic components was also investigated but little improvement in the tenebrescent properties was noted for the majority of additives. In many cases, the added material actually ruined the tenebrescent properties.

A method of fusion in molten media was investigated with moderate results but indications are that a tenebrescent material can be prepared by firing in molten salts.

A tenebrescent glass was prepared by the high temperature firing of a basic composition such as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Some of the glasses could be completely bleached using wavelengths longer than $350 \text{ m}\mu$, some could be bleached only partially and some could not be bleached at all. All the colored glasses could be bleached completely when heated above 300°C . The obtainable color on exposure to ultraviolet was found to vary with composition in some cases.

It appears that the base glass, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, can be modified with regards to its photosensitivity so that different colors and also different degrees of tenebrescent character can be obtained.

Indications are that the material can be used for at least 400,000 cycles and that the proper light sources to be used in conjunction with the memory material could be made available. Limited resolution studies were performed which gave favorable, although inconclusive data, as to the lower limit.

REFERENCE LIST

1. Investigation of Inorganic Phototropic Materials as a Bi-Optic Element Applicable in High Density Storage Computer Memories, Technical Documentary Report No. ASD-TDR-62-305, April 1962.
2. Weyl, W. A., Coloured Glasses, Dawson's of Pall Mall, London, 1959.
3. Kirk, R., "Role of Sulfur in the Luminescence and Coloration of Some Aluminosilicates," Journal of the Electrochemical Society, 101, 9, p. 461-65, 1954.
4. Medved, D. B., "Hackmanite and Its Tenebrescent Properties," American Mineralogist 39, p. 615-29, 1954.
5. Smakula, A., "Color Centers in Calcium and Barium Fluoride," Physical Rev., Vol. 77, p. 408, 1950.

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backmanite type materials and tenebrescent
glass materials are given along with some
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